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LEROUGE, Frederic — Univeriste de Montpellier, 2 July 2002–23 August 2002

Scope of Research

Our research is concerned with some new aspects in the elemento-organic chemistry, including (1) the design and synthesis of novel π-conjugated systems containing main group elements such as boron and silicon for electronic and photonic applications, (2) the synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds and functionalized silyl anions, (3) the elucidation of the σ-conjugation in the polysilane framework using the configuration-constrained oligosilane model systems, (4) the old but new chemistry of the disilapropellane and related compounds, and (5) the development of new efficient reactions using main group element reagents and transition metal complex catalysts.

Research Activities (Year 2002)

Presentations

Boron-Containing π-Electron Systems: Photophysical Properties Control Based on the p_π-π* Conjugation, Yamaguchi S, Shirasaka T, Akiyama S, Tamao K, 5th International Symposium on Functional π-Electron Systems, 30 May - 4 June, 2002, Ulm, Germany.

My 35 Yeas in Organosilicon Chemistry (F. S. Kipping Award Lecture), Tamao K, The 13th International Symposium on Organosilicon Chemistry, 28 August, Guanajuato, Mexico.

Relationship between Photophysical Properties and Conformation of Oligosilanes, Tsuji H, Terada M, Toshimitsu A, Tamao K, 16th Symposium on Fundamental Organic Chemistry, 4 October, Tokyo, Japan.

Grants

Tamao K, Elements Scienece towards Construction of Organic and Inorganic Frameworks Focusing on Quality of Elements, Grant-in-Aid for Scientific Research on COE, April 2000 - March 2005.

Yamaguchi S, Elemento-Organic π-Electron Systems for the Materials Science, PRESTO, Japan Science and Technology Corporation, December 2001 - November 2004.

Awards

Tamao K, Toray Science and Technology Prize, 14 March.

Yamaguchi S, The Chemical Society of Japan Award for Distinguished Young Chemists, Creation of Functional π-Electron Systems Containing Group 13, 14, and 15 Elements, The Chemical Society of Japan, 29 March.

The Disilane Chromophore: Photoelectron and Electronic Spectra of Hexaalkyldisilanes and 1,(n+2)-Disila[n.n.n]propellanes

Photoelectron spectra, solution UV absorption, and magnetic circular dichroism (MCD) of hexamethyldisilane (**1**), hexaethyldisilane (**2**), hexa-tert.-butyldisilane (**3**) and the 1,(n+2)-disila[n.n.n]propellanes [n = 4 (**4**) and 5 (**5**)] were measured, as was the linear dichroism (LD) of **3** and **4** partially aligned in stretched polyethylene. The results support the assignment of the lowest energy electronic absorption band of the disilanes **1** - **5** to a doubly degenerate σ_{SiSi}(HOMO) – π^*_{SiC}(LUMO) transition, and of the next band, observed in the solution spectra of **2** - **4**, and in the gas-phase spectrum of **1**, to a σ_{SiSi} – π^*_{SiSi} transition [1]. MP2/VTZ optimized geometries of **1** - **5** and ab initio calculations of the molecular orbital energies (HF/VTZ//MP2/VTZ) and

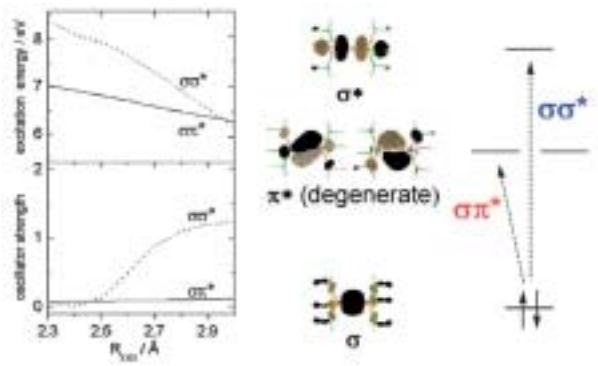

Figure 1. Excitation energy and oscillator strengths of disilane together with their molecular orbitals.

ionization potentials (ROVGF/VTZ//MP2/VTZ) of these disilanes reproduce the reported geometries and the trends observed in the photoelectron spectra, respectively. Calculations of the Kohn-Sham orbital energies (B3LYP/6-31G(d)) and transition energies (TD DFT B3LYP/6-31G(d)) of **1** as a function of Si-Si bond length suggest that many of the trends observed in the UV absorption spectrum of **3**, including the small energy difference between the two transitions observed and the large extinction coefficient of the higher energy (σ_{SiSi} – σ^*_{SiSi}) band are due to its very long Si-Si bond.

1. Casher DL, Tsuji H, Sano A, Katkevics M, Toshimitsu A, Tamao K, Kubota M, Kobayashi T, Ottosson H, Michl J, *J. Phys. Chem. A*, *in press*.

Dibenzoboroles as a New Boron-Containing π-Electron Systems

Boron-containing π-electron systems represents a new class of organic materials with intriguing electronic and photophysical properties due to the p_π-π* conjugation through vacant p-orbital of the boron atom. One notable aspect may be the control of this conjugation which provides an opportunity to modify their properties. In this report, we have succeeded in the synthesis of a series of dibenzoborole derivatives with various groups such as (*N*,*N*-diphenylamino)phenyl, thienyl, and bithienyl groups at the 3,7-positions and have studied their photophysical properties. These new π-electron systems show significant solvatochromism in the fluorescence spectra (Figure 2a) [2]. Thus, about 100-140 nm blue shifts in the emission maxima and 20-30 fold increments in the quantum yields are observed by changing the solvent from THF to DMF. Similar fluorescent changes are observed upon the addition of n-Bu_4NF to their THF solutions, demonstrating their sensing abilities toward a fluoride ion. These fluorescence changes result from the "on/off"-control of the p_π-π* conjugation in their LUMO by the coordination of donor solvents or fluoride ion to the boron atom in the dibenzoborole skeleton (Figure 2b).

2. Yamaguchi S, Shirasaka T, Akiyama S, Tamao K, *J. Am. Chem. Soc.*, **124**, 8816-8817 (2002).

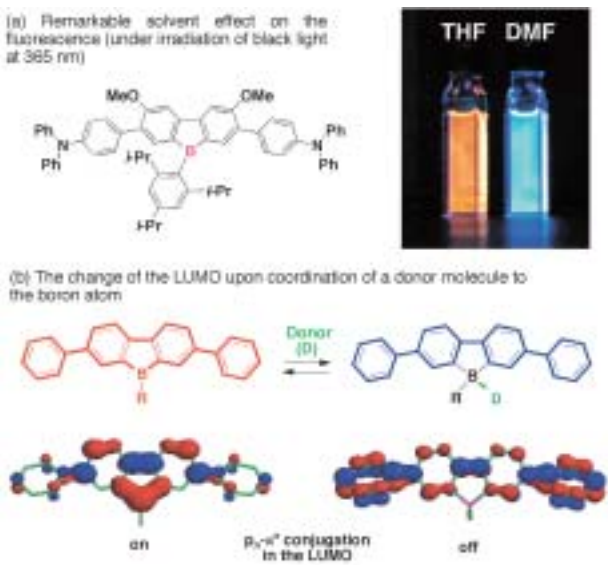

Figure 2. The ON/OFF control of the p_π-π* conjugation in the dibenzoborole-containing p-electron systems.

Tamao K, F. S. Kipping Award, The American Chemical Society, 9 April.

Shirasaka T, Symposium Poster Award, 49th Symposium on Organometallic Chemistry,Japan, Dibenzoborole-Based π-Electron Systems: Synthesis, Photophysics, and Sensing Ability for Fluoride Ion, Kinki Chemical Society, 13 September 2002.